

## Chapter 9

# Fire Protection of Timber Building Structures and Constructions

**Abstract** This chapter presents the industrial approach to improve the fire resistance and fire safety of timber constructions. A comparison analysis of the efficiency of two types of fire protection of timber constructions based on surface and deep impregnation of timber by novel fire-retardant impregnation compositions and based on novel intumescent coatings from plant raw material is presented.

The method of modification of plant raw material and some physicochemical characteristics of product are presented. The effect of fire protection on charring parameters of wood species at standard fire regime is discussed.

The world's developed countries have adopted common principles of fire safety of building structures and constructions aimed first of all at protecting human life and health, as well as minimizing material damage from fire. The fire safety system of building structures involves fire protection measures at their design, construction, and operation stages. Fire protection measures applied in practice are aimed at reducing the risk of fire onset and spread. These measures depend on the fire resistance class and structural fire safety of buildings and their functionality.

Fire safety and fire protection measures for building structures and constructions are conventionally subdivided into active and passive. The first group includes space planning and design solutions developed at the building's design stage with regard for its function (processes taking place in the building) and fire resistance class. Thorough consideration is given to safe evacuation of people and constraining fire spread beyond its seat by fire barriers and smoke control.

Active fire protection measures for building structures and constructions at the operation stage include provisions for early fire detection by various detectors, fire alarm, and notification to alert occupants of fire. Manual and automatic fire-extinguishing devices are to be used to suppress fires in premises at the initial stages.

Passive measures involve the use of various fire protection means and materials. As practice shows, in most cases, the use of fire protection is a cost-effective way to increase the fire safety and fire resistance of constructions. These same measures with reference to timber building structures and constructions are addressed below.

## **9.1 Recent Ways and Means of Fire Protection to Increase Fire Safety and Fire Resistance of Timber Building Constructions**

Fire safety and fire resistance of building structures are the basic parameters that determine the stability of building structures and constructions during a fire. Stability is understood as retention of load-bearing capacity of constructions and structural integrity of a building facility and preservation of its functionality. Fire protection of building structures takes into account their design features and properties of constituent materials, as well as operating conditions.

In buildings and structures with constructions of solid timber or glued laminated timber (glulam) materials with load-bearing and enclosing functions, there are different approaches to enhancing stability and protecting the structures from collapsing during a fire.

If massive load-bearing timber frames of logs, beams, or multilayer glulam materials are employed, then increasing their cross section is one way to enhance their fire resistance rating (see Chap. 8). The optimal necessary dimensions of structural members may be calculated at the design stage if taken into account the charring rate and depth, preserved part of the cross section during a specific period of fire, and changes in mechanical properties of timber during heating.

The main lines of passive fire protection include the use of structural fire protection; impregnation of timber with fire-retardant compositions; direct application of fire-resistive coatings on the material surface, including intumescent types; and the use of combined fire protection.

Combined (integrated) fire protection is an optimal combination of structural fire protection with intumescent fire-retardant coatings or a combination of different types of structural fire protection, e.g., a combination of sheeting and thermal insulation.

The structural fire protection enhancing fire safety and fire resistance rating of timber constructions is similar to fire protection of load-bearing structures and enclosures made of metal, concrete, or reinforced concrete.

Slab and coiled materials, fire-resistive coatings, and inorganic thermal insulation, as well as various types of timber-based panels, are used for this purpose. The main purpose of these claddings is to slow down the heating of protected timber constructions to critical temperature when active pyrolysis starts and timber ignites. They are also supposed to decrease the timber charring rate and heating of its remaining unaltered part beyond the charring front to the limiting temperature responsible for the loss of mechanical properties of timber. The efficiency of timber fire protection by these structural methods depends in the first place on the resistance against fire action and the heat insulation capacity of the fire-resistive materials being used.

Combined fire protection is especially promising in terms of enhancing fire safety and fire resistance of light frame timber buildings.

It is assumed that in standard temperature fire conditions, timber starts to char at 270–300 °C. Experience shows that timber heating beyond the charring front under these conditions is close to the hyperbolic law for cross-sectional temperature changes, whereas mechanical properties decrease linearly with temperature.

When the integrity of structural fire protection is broken due to cracks or delamination, its effect on the timber charring rate is minimized. And in case of global failure of fire protection, it could even turn negative.

Specifications and trademarks of currently used fire protection means, cladding, and heat insulation materials for timber structures are given in works (Romanenkov and Leveetes 1991; Strakhov et al. 2000; Korolchenko and Korolchenko 2006; Leonovich and Sheloumov 2002). The cheapest ones are dry gypsum plasterboard types domestically produced on a large scale: gypsum board (GB) and gypsum-fiber board (GFB).

Structural methods may notably increase the fire resistance rating of timber constructions. However, the fire-resistive materials must be fairly thick, usually more than 10–15 mm.

It was found by experiment, for example, that in a standard fire temperature regime, the time before charring onset,  $\tau_0$ , for solid timber constructions fire protected by with semirigid slab of glass mineral cotton wool (GOST 9573-89) 50-mm thick was 30 min (Strakhov et al. 2000). The fire resistance rating of timber partitions with double-sided GFB cladding was 28 min (Strakhov et al. 2000). Increasing the number of layers or thickness of fire-protective material raises the fire resistance rating of a timber construction.

Typical modern slab materials employed for fire protection of timber constructions include slabs based on cement–silicate binders (Promatect-L), liquid–glass-based vermiculite slabs (PVTN, Ecoplast), noncombustible basalt fiber slabs (PNTB), and rock wool slabs (CONLIT-150).

Thermal calculations of fire resistance of glulam with the indicated structural fire protection means show the effect of fire-resistant material thickness on the increase in time before charring onset,  $\tau_0$ , and reduction of average timber charring rate for a specified period of heat exposure (Table 9.1) (Roytman et al. 2013).

For example, the use of 40-mm-thick vermiculite slabs PVTN increases the  $\tau_0$  value to 106.7 min, reducing the average charring rate of glulam from 0.73 for unprotected items to 0.3 mm/min. Light plaster SOTERM-1M, a material based on a light porous filler and mineral binder, is quite effective.

Calculations of the required thickness of structural fire protection for various load-bearing structures and enclosures made of solid timber or timber-based materials are based on the use of mathematical models that take into account the features of heat and mass transfer during a fire within a “fire protection – construction being protected” system (Strakhov et al. 2000; Roytman et al. 2013). In the process a concept is applied, which states that charring reduces the effective cross section of a timber construction and its strength properties at elevated temperatures and a layer with zero strength is formed in close proximity to the charring front. It was assumed that the timber layer with zero strength was 5-mm thick. Calculations of

**Table 9.1** Time before charring onset and average charring rate of glulam with various means of fire protection

No	Means of fire protection	Thickness, mm	$\tau_0$ , min	$\nu_{av}$ , mm/min in time span of, min	
				30	45
1	Without fire protection	—	4	0.73	0.65
2	Cement–silicate slab Promatect-L	10	15.5	0.67	0.61
		20	35.5	0.58	0.54
		30	60.8	0.52	0.49
3	Vermiculite slab PVTN	10	16.0	0.52	0.49
		20	38.5	0.4	0.38
		30	68.9	0.32	0.31
		40	106.7	0.3	0.29
4	Basalt fiber slab PNTB	20	33.0	0.4	0.38
		30	53.1	0.33	0.31
		40	73.2	0.3	0.29
5	Rockwool slab CONLIT-150	20	35.2	0.43	0.39
		30	54.5	0.36	0.32
		40	74.3	0.32	0.3
6	Coating SOTERM-1M	10	21.5	0.53	0.5
		20	54.5	0.41	0.39
		30	99.8	0.32	0.31
7	Intumescent coating PROTERM WOOD	0.6	26.9	0.87	0.78
		1.0	35.1	0.84	0.73
		1.5	41.8	0.8	0.69
		2.0	47.3	0.78	0.67
		1.0	38.5	0.91	0.78
		1.5	44.5	0.89	0.76
		2.0	49.9	0.87	0.74
8	Intumescent coating OGRAKS-V-SK	0.6	22.5	0.66	0.65
		1.0	34.2	0.73	0.71
		1.5	45.0	0.8	0.73
		2.0	53.8	0.87	0.74
9	Intumescent coating OSP-1	1.0	11.3	0.67	0.6
		3.0	40.5	0.55	0.51
		5.0	78.0	0.46	0.44

temperature fields in glulam in a standard fire regime made in work (Garashchenko et al. 2006) showed not only excessive thickness of the layer  $\delta = 5$  mm confined between isotherms 175 and 300 °C and unable to resist the acting load. A tendency was also revealed toward an increase in this layer, when the structural fire protection thickness grows and heat exposure time is prolonged.

European Standard EN 1995-1-2, Eurocode 5 recommends assuming a zero-strength layer thickness under the charred timber layer equal to 7 mm. The question of the effect of structural fire protection on zero-strength layer thickness is addressed in the work (Schmid et al. 2010) with cross-laminated timber (CLT) as a case study.

Thickness of zero-strength layer below char layer for timber members in load-bearing structures depends on fire exposure conditions, configuration of the construction, and strain type in timber member. Technical guideline on fire safety in timber buildings (Ostman 2010) introduces the improved design methods of load-bearing and load-separating timber structures and presents the effect of different factors on sizes of charring layer and zero-strength layer resulting in standard fire regime.

Fire resistance of timber member is increased with using fire-resistive structural panels or fire-protective intumescent coatings. The efficiency of timber protection depends on the thickness and durability of the coatings. Therefore, fire protection means for timber can be devised on two groups: (1) fire retardant means reducing the spread of flame over a surface and (2) fire resistive means reducing the rate of charring.

Fire protection of timber constructions by surface and deep impregnation with special compositions containing fire retardants, as well as application of fire-retardant coatings, is popular today (Romanenkov and Leveetes 1991; Strakhov et al. 2000; Korolchenko and Korolchenko 2006; Leonovich and Sheloumov 2002; Ostman 2010; Leonovich 2003; Bazhenov et al. 1999; Deyeva 1999; Tychino 1999, 2003). The use of thin-layer intumescent fire-retardant coatings is especially attractive. Even when relatively thin, they demonstrate high fire protection efficiency, and allow the use of modern mechanized methods of application on the item being protected, while retaining the basic texture of the timber and its esthetic appearance.

As a rule, fire-retardant impregnation compositions and coatings for timber are multicomponent systems. Each component of the system has its function in providing the total fire-protective effect and required performance properties.

In most cases, impregnation compositions are salt solutions in water medium or in organic solvents. Surface impregnation is done by multiple manual or mechanized applications of the composition on the timber surface and materials being protected.

Surface impregnation is cheap and versatile but is less effective than deep impregnation. It is attractive because it may be used to protect already installed timber structures directly at a construction site. However, it is very difficult to obtain reliable timber protection by this method. This is mainly due to poor penetration of salts into timber, requiring high salt consumption. Deeper penetration in the surface timber layers is provided by such impregnation methods as hot-and-cold bath and treatment in industrial apparatus – autoclaves with incremental pressure buildup or alternation of vacuum and increased pressure.

The hot-and-cold bath method is used as the principal method of construction timber impregnation in a number of woodworking plants (Novitsky and Stogov 1959). Deep impregnation with fire-retardant salt solutions is based on the characteristics of the capillary-vascular structure of timber. A series of bottlenecks in technology, the high consumption of fire retardants, and the need for specialized equipment for deep impregnation constrain the practical use of this timber fire protection approach.

Today, many impregnation compositions for timber have been developed, which have different sets and proportions of low-molecular inorganic substances and derivatives of organic compounds demonstrating fire-retardant properties. Academic and practical research in this field continues with the objective of finding still more effective fire-retardant compositions for timber and improving the performance properties of the end product.

The substances frequently used in formulas of fire-retardant impregnation compositions include various derivatives of phosphoric and phosphonic acids: mono- and diammonium phosphates and mixtures thereof (ammophos) urea-, melamine-, and amidophosphates and amidomethylphosphonates. Boric acid, ammonium and sodium tetraborates, ammonium salts of sulfuric and hydrochloric acids, chlorides of alkaline-earth metals and polyvalent transition metals, sodium and potassium carbonates – this is by no means a complete list of inorganic substances used as components of fire-retardant impregnation compositions for timber.

Many of the indicated substances have a polyfunctional effect on the chemical constituents of timber. For example, they have the properties of catalysts for etherification of both hydroxyl-containing macromolecules of timber components by phosphorus acids and of agents of cellulose dehydration. In this way, they promote directional change of timber thermal decomposition reactions toward reduction of flammable volatiles through increased yield of char residue. Ammonia and hydrogen chloride generated in thermal decomposition of the employed salts may function as inert flame diluents and inhibitors of radical oxidation reactions in the gas phase. As the temperature rises, the product of thermal decomposition of phosphoric and phosphonic acids derivatives – orthophosphoric acid – turns into pyro-, tri-, and polymetaphosphoric acids, which have low volatility. Upon melting they may form a glassy protective layer on the charred surface. It works as a physical barrier against oxygen diffusion into the carbonized product. An important feature of phosphorus compounds is their unique ability to suppress smoldering combustion reactions in timber. Boric acid and other boron compounds have a similar effect.

The above-mentioned substances making up part of impregnation compositions are hygroscopic and soluble in water. That is why in an atmospheric environment with moisture above 70 % or in direct contact with water, the fire protection efficiency of timber impregnations may be totally or partially lost. To prevent this, it is recommended to apply additional water-resistant covering varnishes and paints or use fire-protected timber materials only inside the buildings.

In terms of enhancing the resistance of materials against moisture, the double impregnation method consisting in consecutive treatment of a timber surface with interacting salt solutions is worth noting. As a result, insoluble or poorly soluble fire retardants are formed in the near-surface timber layers (Romanenkov and Leveetes 1991; Strakhov et al. 2000; Gorshin and Maximenko 1977). For example, consecutive treatment of a surface with solutions of calcium chloride and diammonium phosphate produced moisture-resistant materials (Gorshin and Maximenko 1977).

Another way to enhance moisture resistance of fire-protected timber is introduction of organic and organoelemental substances with low viscosity and

water-repellent properties into impregnation compositions. Organosilicon fluids (Baratov et al. 1988) are of great interest in this context.

An important line in creating modern fire retardants for timber is the development of a new generation of bio-protective and fire-retardant impregnation compositions with partial or full substitution of salt components (Leonovich and Sheloumov 2002; Leonovich 2003; Tychino 2003). Thus, the new-generation biocide Mipor based on water-soluble ethers of phosphorous acid with broad bio-protective action against mold and wood-destroying fungi has proved quite effective. Timber impregnation with Mipor in conjunction with oligomeric organosiloxanes not only provides bio-fire protection of timber but also increases moisture and water resistance of fire-protected timber with retention of the high mechanical parameters of the initial timber (Pokrovskaya et al. 2009; Pokrovskaya and Naganovsky 2004).

Several certified bio-fire-retardant compositions that are widely used in domestic house-building are also worth mentioning. For example, the inner surfaces of timber and glulam constructions in all types of buildings (attic structures, roof frames, voids between walls and cladding) are treated with Pirilax, Attic, and Latic-KD.

Analysis of the situation with research on new lines in the development of impregnation compositions for timber shows continuous endeavors by developers of timber fire retardants to enhance the fire protection effect and limit flame spread over the material surface. This is achieved by increasing the ability of an impregnation composition to form char and expand at the decomposition stage, regardless of interaction with timber components. Another way is to increase the charring rate in the near-surface impregnated layer of timber with the formation of a dense carbon structure and glassy protective layer.

Examples of this approach are the impregnation compositions OK-GF and OK-DS based on orthophosphoric acid, products of carbohydrate hydrolysis, as well as ammonium salts of phosphoric (or sulfuric) acid and dicyandiamide developed in the Republic of Belarus (Tychino 1999, 2003). Low-molecular products of carbohydrate hydrolysis (starch) in this case serve as an additional source of char formation on heat exposure of fire-protected timber, and its expansion occurs at the thermal decomposition stage of the impregnated timber layer.

To lower the fire hazard of timber and other organic materials, a new generation of water-soluble oligomeric fire retardants, which contain elements of both phosphorus and boron in their macromolecules, has been proposed. Their synthesis is based on the reaction of dimethyl phosphite and boric acid with different mole ratios of reagents and temperatures. Treating pine timber with the water composition of P- and B-containing fire retardant increases the oxygen index of the timber from 20–23 to 53 (Bondarenko et al. 2009).

Another example is the development of the fire-retardant composition KSD-A (grade 1) by Lovin-Ognezashchita in collaboration with the SFS Academy. It was shown that the introduction of dihydroxyaromatic compound in an optimal proportion with diammonium phosphate into the impregnation composition enhances charring of the near-surface layer of timber and effectively protects its lower layers (Bondarenko et al. 2009).

The fire-retardant properties of impregnation composition KSD-A will be given in more detail below. Meanwhile, we note that laboratory small-scale GOST R 53292-2009 is the principal method currently used in Russia for evaluating fire-retardant efficiency of the newly developed impregnation compositions and coatings for timber. In situations when the material is exposed to intensive radiative heat flows, fire protection with impregnation compositions may prove to be inefficient. There are cases where timber specimens treated with impregnation compositions were classified among materials with the highest group 1 of fire protection efficiency. However, they showed rapid flame spread over timber surface during the test as per the standard method of GOST 12.1044-89. Therefore, we think the small-scale method of GOST R 53292-2009 may be considered an express method for evaluating fire protection efficiency at the creation stage of novel fire retardants for timber. Solving the practical problems of fire protection of timber-based constructions, cladding, and finishing materials for timber requires full information on all basic fire safety parameters of the recommended fire-protected timber materials. This conclusion is equally valid for all timber fire protection means with the use of both impregnation compositions and coatings.

Intumescent coatings, whose protective properties are revealed on exposure to high temperatures and fire, have a special place among currently used fire retardants. Development of this line of timber fire protection is being widely pursued both in this country and abroad.

Intumescent coatings must contain the following important components: (1) film binders that are simultaneously sources of the carbon skeleton at decomposition; (2) catalysts of carbon skeleton formation reactions; and (3) expansion (intumescence) agents. Various additives capable of influencing the technological, heat-shielding, and other performance characteristics of coatings are introduced to enhance the overall fire-retardant effect. These include fillers with the properties of fire retardants, thickeners, pigments, stabilizers, etc.

The following thermoplastic polymers are recommended as binders acting as the source of carbon skeleton formation: polyvinyl acetate, polyvinyl alcohol, chlorinated polyvinyl chloride, chlorinated rubber, latexes of copolymers of vinyl chloride with vinylidene chloride, chlorosulfonated polyethylene, and polyurethanes.

Urea-formaldehyde, phenol-formaldehyde, dicyandiamide-formaldehyde, and epoxy resins, which form the greatest number of cross-links during curing, are frequently used as thermoreactive polymers. Intumescence of paint coatings requires the transition of a polymer into a plastic, viscous elastic state. Rapid curing of thermoreactive polymers breaks the synchronism with the processes of formation and emission of incombustible vapors and gases as a result of thermal decomposition of expanding agents. Breaking this synchronism prevents the formation of an intumescent coating during heating.

The additional introduction of low-molecular sugars, polyatomic alcohols (e.g., pentaerythritol), and polyatomic phenols into the organic binder increases the yield of carbonized product.



A combination of organic binders and liquid glass is also used for intumescent fire-retardant coatings. For example, the Ekran coating comprises sodium water glass and urea-formaldehyde oligomers. The OSP-1 coating is based on a combination of polyvinyl acetate and liquid glass.

Catalysis of carbon skeleton formation reactions in thermal decomposition of organic binders occurs when there are substances through which strong acidic dehydration and dehydrochlorination agents, cyclization of the formed fragments with unsaturated cyclic olefinic bonds, and cross-linking reactions appear in the system. These substances include the above-mentioned ammonium salts of phosphoric and polyphosphoric acids, sulfates, and other compounds used in fire-retardant impregnation compositions for timber.

These same derivatives of various acids serve as effective intumescent agents for coatings by emitting a lot of incombustible gases ( $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ). High-temperature gas developing agents, such as dicyandiamide, melamine, and melem (e.g., as in the VPM-2 coating (Strakhov et al. 2000)), may be introduced into intumescent coating formulas in an independent state.

These intumescent agents belong to typical gas developing agents, which generate incombustible vapors and gases as a result of chemical decomposition reactions when the substances are heated. Physical agents that generate intumescent fire-retardant coatings include vermiculites and thermally expandable graphites. Vermiculites are laminated mineral compounds that expand and increase in volume when heated. Thermally expandable graphites are intercalation-laminated compounds of natural graphites. Delamination and expansion of graphite particles occurs when they are heated.

Depending on the method of intercalated compound's production and intensity of heating exposure, 300–400-fold intumescence of the substance may be achieved (Fialkov 1997).

The intumescence coefficient of coatings with thermally expandable graphites also depends on their content in the overall coating composition. It was shown, for example, that intumescent coatings based on thermally expandable graphites and organic binders, i.e., urea-formaldehyde oligomers (VPM-2<sup>1</sup>) or chlorosulfonated polyethylene (SGK-1), had intumescence coefficients in standard fire regime providing 7- and 25-fold increases in thickness (Strakhov et al. 2000). The OGRAKS-V-SK coating based on chlorosulfonated polyethylene rubber and thermally expandable graphite has intumescence coefficient 44.

Experimental studies on the effect of fire-retardant coatings on fire resistance rating and fire hazard class are very limited. The results of experimental work on glulam fire protection with the intumescent coatings PROTERM Wood and Phoenix DP (Garashchenko 2006) are of great interest.

Firing tests were performed on glulam panels made of pine Grade II boards with cross section  $30 \times 127$  mm with above fire protection according to the standard temperature regime as per GOST 30403-96.

The test apparatus included a combustion chamber with standard temperature regime and a heat chamber with the temperature regime set according to the following time dependence:

$$T_f = T_0 + 200 \log (8\tau + 1), ^\circ\text{C}$$

Five layers of the transparent intumescent varnish coating PROTERM WOOD based on a water suspension of expansion agents, fire retardants, and other specific additives in polyvinylchloride latex were applied on the surface of glulam panels with total composition consumption of  $1.8 \text{ kg/m}^2$ . The coating was 1–1.2-mm thick. Covering varnish PROTERM WOOD TOP A1 was applied with the consumption of  $0.05 \text{ kg/m}^2$  to increase water resistance. Independent tests of the fire hazard parameters of fire-protected timber specimens showed that they belong to Groups G1, V1, and D1; i.e., they are weakened combustible, hard flammable materials with low smoke generation capacity.

It was found that active intumescence of the PROTERM WOOD coating in the combustion chamber started from the 3rd minute at a temperature of  $100\text{--}140^\circ\text{C}$ . Its thickness increased 100-fold in 20 min, when the maximum intumescent layer thickness of 120 mm was achieved. A reduction in the intumescent layer thickness due to burn-off was recorded on from the 25th minute of the test. By this time, timber surface charring had started (a temperature of  $300^\circ\text{C}$  was registered). The specified temperature of  $300^\circ\text{C}$  at a depth of 2 mm was achieved only in 31–32 min. Charring zone propagation on the specimen surface in the heat chamber in this period was less than 50 mm. The conclusion after the firing tests was that the fire-retardant coating PROTERM WOOD provides fire hazard class K0 (30) for glulam.

Intumescent coating PHOENIX DP with covering varnish PHOENIX DP TOP also demonstrated high efficiency of glulam fire protection. It differed from PROTERM WOOD in the proportion of PVC latex components and by the presence of some additives. It was applied on glulam panels in three layers with total average consumption of  $1.0 \text{ kg/m}^2$  that provided a coating thickness of 0.6 mm. Glulam specimens with PHOENIX DP coating were assigned to Groups G1, V1, D2, and T2 by fire hazard parameters with consumption of  $320 \text{ g/m}^2$ .

Visual examination of the behavior of fire-retardant coatings in the combustion chamber showed that intumescence of the PHOENIX DP coating starts from the first minute and proceeds intensively at  $110\text{--}140^\circ\text{C}$ . By the 17th minute, the thickness of intumesced layer reached 60 mm as a result of a 100-fold increase in the coating thickness. Its reduction as a result of burn-off was observed after 20 min of fire action. Glulam surface charring was registered at the 27th minute, but a temperature of  $300^\circ\text{C}$  at a 2-mm depth in the glulam was not achieved during the 30 min of the test. A similar result was attained in the heat chamber. Therefore, a 0.6-mm-thick layer of intumescent coating PHOENIX DP secures fire hazard class K0(30) for the glulam load-bearing constructions (Garashchenko 2006).

The obtained experimental confirmations of the high efficiency of glulam fire protection by intumescent coatings based on organic polymers are in agreement with thermal calculations of their fire resistance (Garashchenko et al. 2006).

Intumescent fire-resistant coatings have complex behavior in fire conditions. Mathematical modeling of the performance of intumescent fire-resistant coatings and the calculation procedure are given in monograph (Strakhov et al. 2000). Calculation of the optimal thickness for these coatings for effective protection of building constructions requires information on many fire protection characteristics. Along with the thermophysical and thermochemical properties of the material, it is important to know the temperature parameters of its state and decomposition, properties of the coating components, and the dependence of thermal conductivity and specific heat on temperature. As numeric calculations of the mathematical model show that the fire protection efficiency of intumescent coatings depends on three parameters: intumescence coefficient of the coating, radiative heat transfer parameter, and mass loss parameter, which characterizes the stability of char foam. These parameters are defined experimentally and by calculation, on the basis of detected temperature fields in the protected material (Strakhov et al. 2000).

As we have already noted, with few exceptions, the efficiency of timber fire protection by novel intumescent impregnation compositions and coatings is assessed by mass loss during tests on specimens as per GOST R 53292-2009 (Afanasyev et al. 2007; Balakin et al. 2007; New generation of fire protective compositions for timber 2000). To what extent these fire retardants reduce the main parameters of timber fire hazard is unclear. How closely do the data on Group 1 or 2 fire protection efficiency obtained by this method agree with the fire hazard parameters of materials under more intensive radiative flows? Is there any relationship between efficiency and the fire-retardant mechanism of impregnation compositions and intumescent coatings? These questions are of great practical interest.

In foreign practice, fire protection efficiency of impregnation compositions and coatings for timber is mostly assessed by comprehensive tests using laboratory cone calorimeters (ISO 5660, ASTM E1354). This method makes it possible to determine the mass loss rate, heat release parameters (maximum and average heat release rate, total heat release in a certain period), effective combustion heat and smoke generation capacity, toxic gas output, and other parameters. Fire protection efficiency is also assessed by the medium-scale SBI method (EN 13823). It is used to classify building materials by fire hazard. The basic parameters are heat and smoke release (FIGRA, SMOGRA).

For example, the ISO 5660 method was used to prove the high fire protection efficiency of an intumescent coating based on urea–dicyandiamide–formaldehyde resin in combination with mono- and diammonium phosphate and dextrin. Pine specimens with the coating tested for 30 min under a radiative heat flow of 35 kW/m<sup>2</sup> showed neither ignition nor mass loss, nor heat release. After ignition, the maximum heat release rate was almost twofold lower compared to the original timber. The time to reach peak heat release rate, which marks the onset of intensive charring, increased (Wladyka-Przybylak and Kozłowski 1999).

It was interesting to compare the efficiency of two novel fire protection systems for timber belonging to diverse compound classes by molecular structure and

chemical composition. The test program was aimed at determining the factors affecting timber fire protection efficiency, as well as revealing the possible fire protection mechanism of the two systems.

The first fire protection system involved impregnation compositions based on low-molecular substances, i.e., KSD-A compositions. The second system involved intumescent film binders based on modified plant raw materials not containing additional flame retardants.

## 9.2 Novel Fire-Retardant Impregnation Compositions for Treatment of Timber Products

The novel impregnation compositions for surface treatment of timber constructions manufactured by Lovin-Ognezashchita Research and Production Company under the common name KSD-A are balanced synergetic mixtures with fire-bio-protective functions. KSD-A compositions of grades 1, 2, and 3 are environmentally safe and designed for surface treatment of interior timber constructions. If they are applied under external atmospheric exposure, it is recommended to use additional moisture-protective Biox-Universal textured coating.

An initial assessment of the fire protection efficiency of impregnation composition KSD-A (grade 1) according to the standard method of GOST R 53292-2009 showed that Group II fire protection efficiency is provided after only one layer was applied on a timber surface with consumption of 100–180 g/m<sup>2</sup>. Mass loss during firing tests of timber specimens was 8–5.5 % in this case. Guaranteed service life of fire protection (in enclosed premises) is 10 years. Fire-retardant compositions KSD-A (grades 2, 3) with consumption of 240–300 g/m<sup>2</sup> provide Group II fire protection efficiency with a service life guarantee of 3 years. KSD-A compositions of grades 1 and 2 give the timber a beige color. Grade 3 does not color the timber and is recommended for bio-fire protection treatment of the surface of timber constructions with elevated esthetic requirements.

A further comprehensive study of the fire hazard characteristics of timber specimens with fire protection treatment by KSD-A (grade 1) was carried out by standard methods. Ignition parameters and mass burn-off rate were determined with external heat flow of 18–50 kW/m<sup>2</sup> in the unit as per GOST 30402-96. Flame spread, smoke generation capacity, and toxicity of combustion products were determined as per GOST 12.1.044-89, pp. 4.19, 4.18, and 4.20. Modern physical and physicochemical analysis methods (scanning electron microscopy, dynamic thermogravimetric analysis, IR spectroscopy and others) were employed to identify the leading mechanism of action of the fire-bio-protection impregnation composition.

Table 9.2 shows the results of a study of the effect of impregnation composition KSD-A (grade 1) on ignitability and maximum mass loss rate of pine timber.

**Table 9.2** Effect of the fire-retardant impregnation composition KSD-A on ignitability and mass loss rate of timber

Specimen	Consumption, g/m <sup>2</sup>	$q_e$ , kW/m <sup>2</sup>	$\tau_i$ , s	$q_{cr}^i$ , kW/m <sup>2</sup>	MLR <sub>max</sub> <sup>a</sup> , g/m <sup>2</sup> s
Pine	–	30	21	12.5	–
	–	40	9		28
	–	50	4		35.7
Pine with impregnation composition	300	30	195	22.5	–
		40	39		–
KSD-A (g.1)		50	16		21.3
		400	30	600	25.0
			40	72	–
			50	29	14.4

<sup>a</sup> $q_e'' = 50$  kW/m<sup>2</sup>

Quantitative flammability parameters that allow to compare timber fire protection effects are ignition delay time,  $\tau_i$ , at a specified external heat flow density,  $q_e$ ; critical ignition heat flow,  $q_{cr}^i$ ; and also maximum mass loss rate, MLR<sub>max</sub>.

Surface treatment of timber with the fire-retardant composition KSD-A increases its resistance to ignition by many times. Not only does the ignition delay time of the specimens lengthen, but the values of critical heat flow needed to ignite them also increase.

With increased consumption of fire-retardant composition, the maximum mass loss rate during specimen combustion is more than halved compared to untreated timber, even under very severe conditions of radiative heat flow exposure ( $q_e'' = 50$  kW/m<sup>2</sup>). Therefore, the fire-retardant compositions affect the timber pyrolysis profile by slowing down and reducing the formation and emission of flammable volatiles. The quantity and quality of the char layer formed on the specimen surface is of considerable importance.

As an analysis of electron microscopy replicas from the specimen surfaces showed, the structure of the surface layer changes noticeably when the timber is treated with impregnation composition KSD-A. The surface of an untreated specimen had typical elements of coniferous timber structure: ribbon-shaped microfibrils and fibers bordered by round pores. After impregnation with KSD-A (grade 1), the pores were no longer visible, and transverse formations – chords – were seen in space between the microfibrils. The whole thing looks like a kind of spatially cross-linked structure (Balakin et al. 2007). The dense charred layer formed on a timber surface exposed to fire is more homogeneous in this case and has no deep cracks compared to the charred surface of untreated timber.

The question of the effect of a fire-retardant composition on flame spread (FS) over the timber surface was especially interesting. Table 9.3 shows the data on the variation of basic FS characteristics after surface impregnation of timber with KSD-A composition (grade 1) as a function of its consumption.

**Table 9.3** Flame spread parameters on a fire protected timber surface

Specimen	Composition consumption, g/m <sup>2</sup>	FS index, $I_{FS}$	FS rate at 32 kW/m <sup>2</sup> , mm/s	$q_{cr}^{FS}$ , kW/m <sup>2</sup>
Pine	—	55.0	4.4	5.0
Pine + KSD-A	300	2.5	1.10	19.6
Pine + KSD-A	400	0.5	0.74	22.0

Surface impregnation of timber with KSD-A composition significantly lowers the FS index and FS rate over the timber surface and increases the critical density of radiative heat flow for FS,  $q_{cr}^{FS}$ . Fire-protected timber materials are transferred to the category of slow flame spreading materials, FS1. With increased consumption of the composition, all parameters improve, and the appearance of materials with  $I_{FS} = 0$ , i.e., not spreading flame, may be expected. It should be noted that the flame spread rate at the limit of combustion has a certain value probably due to the minimum critical mass flow rate of flammable pyrolysis product emission needed for FS. All tested specimens, regardless of the registered  $q_{cr}^{FS}$  values, had the same FS rate at the limit of combustion extinction: 0.23–0.24 mm/s.

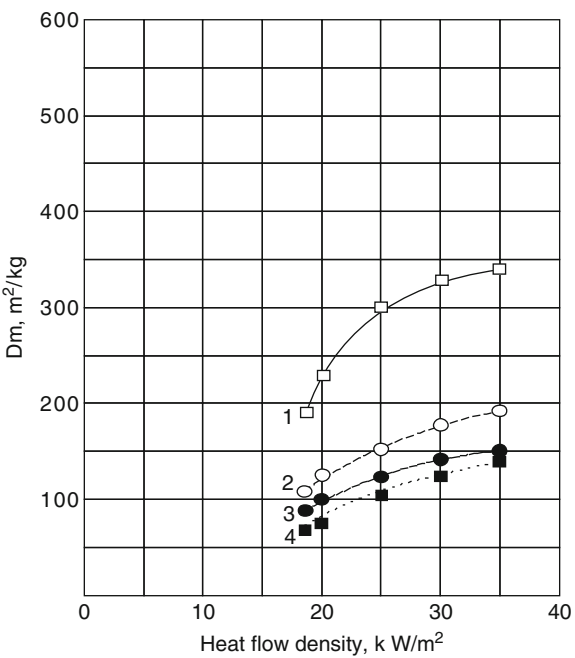
Fire-protective treatment of timber significantly affects smoke generation capacity in timber combustion and toxicity of fuel gases. The optical density of smoke during flaming combustion of timber materials is usually lower compared to smoldering combustion. At the same time, oxygen deficiency in the reaction zone of char smoldering leads to enhanced emission of toxic carbon monoxide. In the most dangerous smoldering timber combustion regime with and without fire protection treatment that was studied, there was a characteristic increase in the smoke generation coefficient as external heat flow density increased from 18 to 35.0 kW/m<sup>2</sup> (Fig. 9.1).

However, in equal test conditions, the fire protected specimens had a lower smoke generation coefficient compared to the initial timber and belong to the category of materials with moderate smoke generation capacity according to the established classification. With impregnation composition consumption of 300 and 400 g/m<sup>2</sup>, the smoke generation coefficient of pine at a heat flow of 35 kW/m<sup>2</sup> is successfully reduced from 345.1 to 195 and 150 m<sup>2</sup>/kg, respectively.

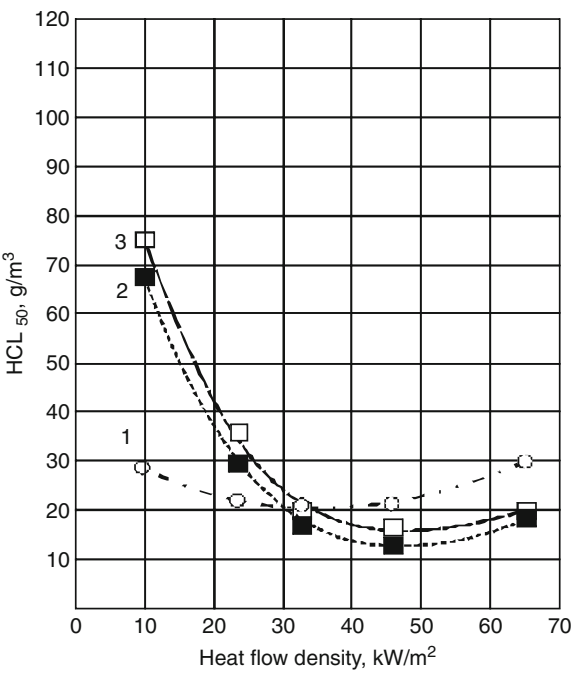
The toxicity of smoldering combustion products of timber depends on external heat flow density. Within a wide range of densities 10–65 kW/m<sup>2</sup>, untreated timber belongs to the group of highly hazardous materials in terms of combustion product toxicity (Fig. 9.2, curve 1).

Curve 1 shows the complex extreme character of the ratio of material combustion product toxicity to external heat flow density. Within the interval of 10–23 kW/m<sup>2</sup>, there is a typical, although slight, dependence of combustion product toxicity increase (decrease in HCL<sub>50</sub> due to enhanced CO concentration). Autoignition of pine occurs at 23–24 kW/m<sup>2</sup> during specimen tests as per GOST 12.1.044-89. As a result, oxidation of carbon monoxide increases, and the toxicity index HCL<sub>50</sub> rises again with the increase in heat flow intensity.

**Fig. 9.1** Smoke generation coefficient of timber with applied compositions vs. heat flow density: 1 untreated pine, 2 pine with KSD-A composition (grade 1) (consumption 300 g/m<sup>2</sup>), 3 pine with KSD-A composition (grade 1) (consumption 400 g/m<sup>2</sup>), 4 pine with starch MP  $\alpha = 0.5$  (consumption 300 g/m<sup>2</sup>)



**Fig. 9.2** Material combustion product toxicity in smoldering regime vs. external radiative heat flow density: 1 untreated pine, 2 KSD-A composition (grade 1) (consumption 300 g/m<sup>2</sup>), 3 pine with starch MP  $\alpha = 0.5$  (consumption 300 g/m<sup>2</sup>)



Timber treatment with a fire-retardant impregnation composition lowers the toxicity of flue gases at external heat flow exposure of 10–20 kW/m<sup>2</sup>. However, it impedes autoignition of timber and expands the range of the smoldering combustion regime. Critical heat flow for autoignition of timber treated with KSD-A impregnation composition with consumption of 300 g/m<sup>2</sup> increases to 44.0 kW/m<sup>2</sup>.

Therefore, surface impregnation of timber with a fire-retardant composition moves timber from the highly hazardous group in terms of combustion product toxicity to the moderately hazardous group at low heat flow intensity. This result leads to the conclusion that even a composition that includes phosphorous does not fully suppress smoldering timber combustion. This may be an indication that the timber pyrolysis front penetrates beyond the charred phosphorous-containing surface layer and that the phosphorous concentration is insufficient to suppress char oxidation.

Deep impregnation of timber with KSD-A composition (g.1) under pressure by the hot-and-cold bath method or soaking in cold solution results in obtaining materials with Group 1 fire protection efficiency. The depth of fire-retardant penetration into the timber and its dry pickup per unit volume increase compared to surface impregnation. Fire safety indices of timber constructions significantly improve. In order to select the optimal regime of deep impregnation with the KSD-A composition, the effect of temperature and pressure in the autoclave and impregnation time was studied. It was found that increasing the temperature from 20 to 60 °C and raising the pressure above 8 atm barely improved the impregnation results. Thus, the optimal and most economical regime is impregnation with KSD-A composition (g.1) at room temperature and pressure of 7–8 atm for 1.5 h without preliminary vacuum treatment of the timber. Dry pickup per unit volume of pine timber in this case was 50 kg/m<sup>3</sup>.

Deep impregnation with KSD-A (g.1) composition by the hot-and-cold bath method with a temperature change from 50–80 (8 h) to 20 °C (16 h) affected the pickup of dry matter. Pickup of 12 kg/m<sup>3</sup> afforded the material Group II fire protection efficiency, while pickup of 32–43 kg/m<sup>3</sup> afforded Group I, and slightly flammable material was obtained. At dry pickup of 50–60 kg/m<sup>3</sup>, there was a stable result of Group I and combustibility characteristics under intensive external radiative heat flow.

Comprehensive testing of timber specimens with deep impregnation with KSD-A composition (g.1) showed that the material became low combustible (Group G1 as per GOST 30244), hard ignitable (Group V 1 as per GOST 30402), flame spread not present (Group FS1 as per GOST 30444-97), with moderate smoke generation capacity (Group D2), and moderately hazardous in terms of combustion product toxicity (Group T2 as per GOST 12.1.044-89, pp. 4.18 and 4.20). These results allow us to define the fire hazard class of fire-protected timber as KM1 – nonflammable material.

In order to assess the structural fire safety class of timber with deep impregnation with KSD-A composition (grade 1), a wall fragment of 200-mm half-logs with dimensions 1,200 × 2,400 mm was constructed.



The half-logs were fastened with  $6 \times 130$ -mm bolt screws on the unheated side. The main parameters for assessing the fire safety of building constructions as per GOST 30403-96 are the dimensions of specimen damage in the heat chamber at standard temperature and the occurrence of flaming combustion or other heat effects in the reference area along the specimen's length. Damage is understood to mean charring, melting, and burn-off of the construction material to a depth exceeding 0.2 cm. Tests of timber specimens with deep impregnation with KSD-A composition (g.1) showed neither flaming combustion nor other heat effects in the heat chamber. Minor damage (charring) to the specimen in the reference area was about 2 mm for a length of 270 mm. It was more of the consequence of the fire protection mechanism KSD-A composition than timber construction burn-off. Deep impregnation of timber with KSD-A composition (grade 1) provides effective fire protection for timber and turns it into class K1(30). Based on the results of accelerated tests, it was found that the guaranteed period of preservation of fire protection properties in timber constructions treated with KSD-A composition (grade 1) by deep impregnation method was 30 years.

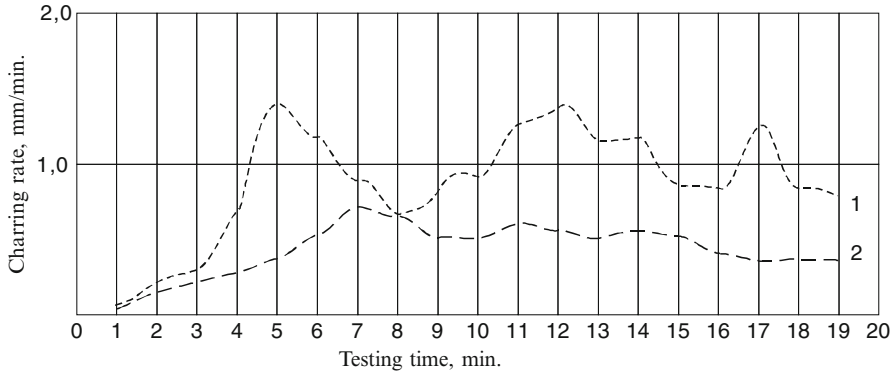
### ***9.2.1 Charring Parameters of Timber Species with Fire-Retardant Treatment at Standard Fire Regime***

The results of thermal analysis and a study of Fourier IR spectra behavior in the surface layers of fire-protected timber specimens during heat exposure have confirmed the important role of char formation in lowering the fire hazard parameters of timber.

The analysis of Fourier IR spectra in the range of 400–4,000/cm focused on areas with a frequency drift of O–H, C–H, and C–O–C bonds in structural units of timber components. These units are especially sensitive to transformations during heat exposure. Increased band intensities caused by the appearance of  $C=C_{\text{AROM}}$  bonds and enhancement of the absorption background indicated active carbonization of the substrate under the effect of the fire retardant. The conclusion was that KSD-A impregnation composition reacts with timber components during heating, speeds up dehydration and molecule cross-linking reactions, and leads to char layer formation with improved heat-shielding properties.

The timber charring rate depends on many factors: intensity and character of external heat flow, oxygen concentration in the environment, timber variety and density, its moisture content, etc. (Mikkola 1991).

A similar approach to that of (Demidov 2005) was used to calculate the charring rate of the near-surface layer in fire-protected specimens. The researchers factored in their own measurements of mass loss rate, temperature in the pyrolysis front and on the char layer surface, thickness and density of the impregnated layer, and average values of gasification enthalpy (Strakhov et al. 2000). For total heat flow (external radiation flow and from flame-generated flow) of  $50 \text{ kW/m}^2$ , the calculated



**Fig. 9.3** Variation of charring rate of pine specimens during tests at standard fire regime temperature: 1 without fire protection and 2 with surface treatment by KSD-A, grade 1 (400 g/m<sup>2</sup>)

**Table 9.4** Effect of treating pine timber by fire-retardant composition KSD-A on the density and thermophysical properties of the char layer

Specimen	$\rho_c$ , kg/m <sup>3</sup>	$d_{av}$ , nm of pores	$T_s$ , K	$\lambda$ , W/mK	$a$ , 10 <sup>4</sup> m <sup>2</sup> /s	$\lambda\rho c$ , kJ <sup>2</sup> /m <sup>4</sup> K <sup>2</sup> s
Pine	268	25.03	1,005	0.32	7.6	0.133
Pine with KSD-A	217	1.98	880	0.093	2.7	0.031

charring rate of the near-surface layer of the timber was 4.67 mm/min. Under these conditions, an untreated pine specimen charred at the rate of 1.39 mm/min. Thus, the fire-retardant composition increases the charring rate of the near-surface layer of the timber by almost 3.5 times. Rapid charring of the surface layer of the timber slows down heating, subsequent pyrolysis, and charring of underlying layers.

A similar effect of fire-retardant composition on the timber charring rate was seen in tests of specimens (150 × 150 × 30 mm) in a laboratory furnace at standard fire regime temperature (Fig. 9.3).

It can be seen that at the first stage of a standard fire, the maximum fire-protected timber charring rate is higher compared to the original specimen. Then the charring rate of fire protected timber decreases drastically. At the end of 20 min of testing, the charred layer in untreated timber was 19-mm thick. The specimen with fire-retardant impregnation charred to a depth of 8 mm during that period. Therefore, the average charring rate of the original pine specimen was 0.95 mm/min, whereas the rate of the impregnated specimen was 0.4 mm/min.

Surface treatment of timber with fire-retardant composition KSD-A (grade 1) not only results in less charring rate of the timber during combustion, it also affects the characteristics of the porous structure and thermophysical properties of the char layer (Table 9.4).

Fireproofing timber with impregnation composition leads to the formation of char with a fine-porous structure, low thermal conductivity, and thermal inertia. This improves the thermal insulating capacity of the char.

### **9.3 Fire Protection Properties of Novel Intumescent Coatings for Constructional Timber Based on Plant Raw Material**

In recent years, the problem of environmental safety in all spheres of human life and activity has become a fundamental issue. The search for environmentally safe and effective fire protection means for timber turned our attention to intumescent systems that do not contain substances and elements toxic and harmful to human health. We were interested in finding out whether organic systems inherent in natural plant raw materials could serve as effective fire retardants for timber and synthetic polymer materials.

This section addresses the fire protection properties of modified polysaccharides from various plant raw materials for improving the fire safety of timber structures.

Modification of plant raw material polysaccharides holds a prominent place in world materials technology. Modified cellulose-based materials are widely known and have practical importance. Today, researchers' attention is turned to the modification of starch-containing plant raw materials. Similarly to cellulose, starch is modified by producing ethers and esters of polysaccharides by  $C_6$  hydroxyl groups, through the formation of grafted copolymers. The suggested methods are partial decomposition or macromolecule cross-linking under the action of physical means, chemical agents, or enzymes (Cellulose and starch esters [2003](#)).

Many years of fundamental researches on selective catalytic oxidation of organic substances carried out in the Semenov Institute of Chemical Physics of the USSR Academy of Sciences and later in the Emanuel Institute of Biochemical Physics of the Russian Academy of Sciences resulted in the development of a new method. This original, one-of-a-kind modification method is based on catalytic oxidation of various carbohydrates by molecular oxygen in alkaline media (Skibida et al. [1996](#)). It turned out that in the presence of copper and bases, high oxidation rates by oxygen are possible not only for alcohols and ketones with a different structure but also for polysaccharides (starches, dextrans, cellulose). The mechanism of this reaction is addressed in work (Sakharov and Skibida [2001](#)).

A distinctive feature of the method is that in mild oxidation conditions (40–75 °C), the backbone macromolecular chains do not break, and selective modification of macromolecule units and fragments takes place, thus maintaining the high-molecular character of natural polymers, which are the basis of plant raw materials. The method is attractive because it solves the refusing problem for both utilization of reject agricultural products and food and forest industry wastes. It makes it possible to obtain a range of inexpensive, environmentally safe water-soluble reagents for various purposes with almost 100 % yield of end product. The

production process is one stage. The production process is nearly waste-free and is energy-saving, because it does not require high temperatures and elevated pressures.

There are many areas of application for plant raw materials modified in this way. It was shown, for example, that products with various degrees of oxidation of starch-containing raw materials are useful as glues and binders in the production of paper, high-quality chipboard, and fiberboard with low toxicity. Oxidized starch reagents are effective as hardening regulators for gypsum and concrete, corrosion inhibitors of ferrous metals, etc. (Sakharov 2005).

Our work is focused on the use of products of oxidative modification of plant raw materials as intumescent fire-retardant coatings for timber. Although there are numerous versions of various products of plant raw material modification (Skibida et al. 2001), the physicochemical characteristics of only one representative specimen are studied in detail – the product of catalytic oxidation of potato starch.

### ***9.3.1 Method of Oxidative Modification of Plant Raw Material and Some Physicochemical Characteristics of the Product***

Common potato starch was with molecular mass  $MM = 10^6$ ; 20 % amylose and 80 % amylopectin were chosen for catalytic oxidative modification of polysaccharides by gaseous oxygen. In its chemical composition, amylose is a linear  $\alpha$ -1,4-D polyglucoside, whereas amylopectin is a branched polymer with  $\alpha$ -1,4-D- and  $\alpha$ -1,6-D-glycoside linkages. Electron microscopy and X-ray diffraction have proved that the structure of a native dry starch granule consists of periodically alternating crystalline and amorphous lamellae formed from fragments of polysaccharide macromolecules. Crystalline regions are formed from side amylopectin chains organized in double helices. Amorphous regions include backbone chains of amylopectin macromolecules with a certain hierarchy of branch points. A significant part of the amylose molecules probably gets into the amorphous region. The specimen used in the test had B-type polymorphic crystalline structure. The degree of crystallinity of potato starch did not exceed 30 %, but the degree of order of polysaccharide macromolecules was higher than the degree of crystallinity of the starch. Catalytic oxidation of starch was performed in the following way.

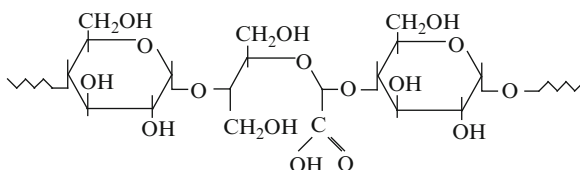
A reactor with a rapid mixer was sequentially charged with water, starch, and catalyst (salt of bivalent copper) at the content of  $5 \times 10^{-3}$  mol/l and alkali 0.5 mol/l. The system was blown by oxygen to drive out the air, then the reaction mass was heated at 75 °C for 6 h. The resulting starch oxidate gel was dried at room temperature, then in vacuum of  $10^{-4}$  Torr to constant weight. Under the adopted conditions, modified starch was produced with oxidation degree of polysaccharides of 0.5, correspondingly – a product with one carboxyl group per 2 polysaccharide molecular units.

**Table 9.5** Effect of temperature on specific heat of oxidated starch polysaccharides

$T, ^\circ\text{C}$	$C_P, \text{J/g deg}$	$T, ^\circ\text{C}$	$C_P, \text{J/g deg}$
10	1.29	90	1.84
20	1.35 (1.25)	100	1.99 (1.65)
30	1.55	110	2.03
40	1.62 (1.34)	120	2.1 (1.76)
50	1.63	130	2.21
60	1.62	140	2.29
70	1.66	150	2.32
80	1.73 (1.53)	160	2.36

Note: The values of  $C_P$  for dry original starch are given in brackets

Various physical and physicochemical methods of analysis were used to determine the chemical composition and structure of the oxidate (Aseeva et al. 2009a). The chemical composition of the oxidated starch polysaccharide can be represented with certainty by the formula:



The employed method differs fundamentally from common oxidation of substances by molecular oxygen, which proceeds by the free-radical mechanism. It should be emphasized that it allows salts of polyoxycarboxylic acids to be obtained directly from polysaccharides of plant raw materials. By varying the ratio of catalyst to base and the cation nature, it is possible to change the properties of carbohydrate oxidation products, including fire protection properties (Skibida et al. 2001).

As a result of partial opening of cyclic anhydroglucose units and carboxylation, oxidate macromolecules should have more freedom of movement and molar volume compared to the initial starch. This factor should affect the physical properties of starch oxidate, for example, specific heat and density. Experimental values of specific heat of dry starch oxidate in the amorphous state in the temperature range of 10–160 °C did indeed turn out to be higher (Table 9.5).

The density of dry starch at 25 °C is 1.50 g/cm<sup>3</sup>. The density of a dry starch oxidate specimen found picnometrically in acetone at 22–25 °C was 1.479 g/cm<sup>3</sup>. The theoretical value of oxidate density at 25 °C in Na-salt form is 1.497 g/cm<sup>3</sup>, whereas in acid form it is 1.439 g/cm<sup>3</sup>. The calculation was done on the basis of

contributions to the molar volume of van der Waals volumes of groups, atoms, and bond lengths in the structural unit of an oxidate macromolecule (Aseeva et al. 2009a). With consideration of the starch oxidation degree, the difference between the calculated and experimental density values is 1.2 %.

To understand the mechanism of foamed char formation and fire-protective action of oxidated polysaccharides, it is important to know the alteration of their physical state and transition types during heating.

DSC results showed that a low-temperature transition from the amorphocrystalline state of polymer starch oxidate to the amorpho-vitreous state occurs within the range of 49–65 °C.

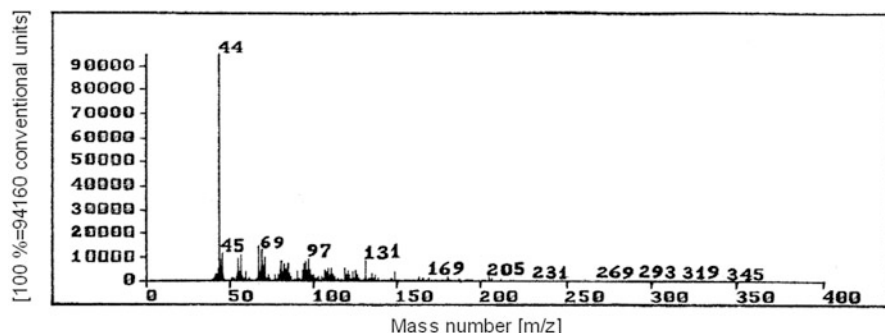
During thermomechanical testing at constant load, there was only slight deformation of the polymer right up to the glass transition temperature  $T_g = 187.7$  °C. Upon reaching the flow temperature  $T_f = 209$  °C, the relative deformation increased very rapidly and at 235 °C reached 100 %. Thus, oxidated polysaccharides exhibit the properties of typical rigid-chain thermoplasts. The interval between flow and glass transition temperatures in the case of oxidate is narrower compared to its original starch predecessor (64 °C).

Oxidative modification of starch lowers the degree of crystallinity of polymer almost twofold. However, the structural parameters of crystallites (length of cooperative melting unit and crystallite thickness) remain almost unchanged, though. We believe this is due to the reduction in the length of amylopectin branch fragments capable of becoming ordered in double helices as a result of hydroxycarboxylate clusters.

A comparison of thermodynamic parameters of crystallites in the structures of oxidate and the initial starch sample allows us to estimate crystallite quality after starch modification. Higher values of surface energy, enthalpy, and entropy of crystallites in the amorphocrystalline structure of polysaccharide oxidate indicate an increase in crystallite imperfection compared to starch crystallites (Aseeva et al. 2009a).

Visual examination of starch oxidate behavior during isothermal heating for 5 min showed that at 235 °C the specimen volume grew eightfold. However, Fourier IR spectra did not reveal any break of backbone polymer chains. All polymer transformations below 235 °C are attributable to intramolecular dehydration reactions. The reactions of decarboxylation and intermolecular dehydration occur only above 235 °C. Therefore, water and carbon dioxide serve as intumescent agents of starch oxidate in the viscous-flow state. Macromolecule cross-linking prevents breakage of chemical bonds of polymer backbone chains and promotes the formation of stable foamed char. The free foaming coefficient of the specimen at 250 °C over 5 min was 32.

Analysis of mass spectra of starch oxidate thermal decomposition volatiles at 200–300 °C confirms the observed effects. In mass spectra of decomposition volatiles at 250 °C and especially at 300 °C (Fig. 9.4), mainly the peak with mass number  $m/e = 44$  associated with the  $\text{CO}_2^+$  ion was recorded. There are no fragments with large mass numbers.



**Fig. 9.4** Mass spectrum of starch oxidate decomposition volatiles at 300 °C

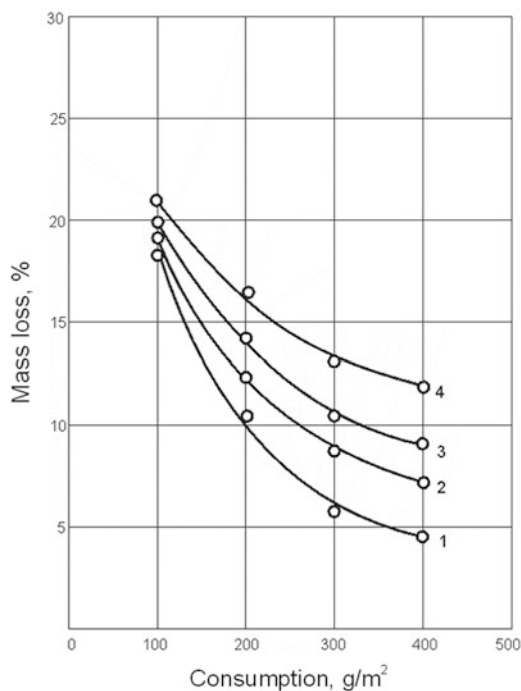
After unfreezing of the polymer's segmental mobility, its active thermal decomposition starts, accompanied by the expansion of the specimen during heating to 280–300 °C and the formation of an insoluble carbonized product with mass yield of about 50 %. Thermal decomposition of starch oxidate occurs as a first-order reaction with parameters  $E_{\text{eff}} = 116.4 \text{ kJ/mol}$  and  $k_0 = 4.3 \times 10^{11} \text{ min}^{-1}$ . At this stage, it proceeds following a mechanism controlled by the reactions of generation of active centers (nucleus) by the law of randomness and by the growth rate of these nuclei (Aseeva et al. 2009a).

Oxidized polysaccharides produced from plant raw material capable of forming foam during heat exposure may be considered environmentally safe high-molecular reagents with the properties of intumescent fire retardants. In fact, these single-component systems perform several competitive functions inherent in the widely known and most effective P-, N-, and/or halogen-containing multicomponent intumescent fire-retardant compositions. In particular, they simultaneously play the roles of binder, film binder and carbon-forming substrate, gas-forming and foaming agent, polymer dehydration, and carbonization reaction catalyst (Skibida et al. 2001).

The complete combustion heat is an important thermodynamic characteristic of starch oxidate. The values of standard higher and lower total combustion heat of the tested specimen in sodium salt form were calculated by the group contribution method (Aseeva et al. 2009a). They are equal to 15.496 and 14.256 kJ/g. The lower total combustion heat had been also calculated by the Mendeleev equation using the experimental results of element analysis. Its value is 14.409 kJ/g, and it differs from the above-mentioned values by only 1 % (Aseeva et al. 2009a). The lower heat of complete combustion of original potato starch according to experimental data is 16.086 kJ/g.

The study results on the efficiency of timber fire protection by intumescent coatings based on catalytically oxidized polysaccharides of starch-containing plant raw material are presented below.

**Fig. 9.5** Mass loss during combustion of timber specimens vs. MP composition and oxidation degree,  $\alpha$ : 1 starch MP,  $\alpha = 0.5$ ; 2 rice MP,  $\alpha = 0.5$ ; 3 starch MP,  $\alpha = 0.3$ ; 4 rice MP,  $\alpha = 0.3$



### 9.3.2 Effect of Modification and Type of Plant Raw Material on Fire Protection Efficiency of Intumescent Coatings for Timber

The plant raw materials used for modification by catalytic oxidation method not only included potato starch, but also cornstarch and tapioca starch, as well as rice grits – food industry waste (hereinafter referred to as just rice). Products with various degrees of oxidation were produced by changing the proportion of catalyst and base.

When water-based compositions of modified polysaccharides (MP) are applied on a timber surface, transparent homogeneous coatings with good adhesion are formed due to the presence of hydrophilic groups in oxidate macromolecules and their structural affinity to the basic timber components.

Fire protection efficiency of intumescent coatings for timber based on oxidated polysaccharides is affected not only by coating thickness due to fire-retardant composition consumption, but also by such factors as degree of catalytic oxidation of polysaccharides and the source of plant raw material. This is clearly seen if we compare the fire protection effect of modified potato starch and rice according to the GOST R 53292-2009 standard (Fig. 9.5). At the same time, the difference in fire protection efficiency of potato, corn, and tapioca starch oxidates with the same modification degree was insignificant. Rice grits probably contain some other substances besides starch.



**Table 9.6** Effect of  $q''_c$  on the characteristics of the char foamed layer formed on a timber surface with MP coatings

Type of MP	$q''_c$ , kW/m <sup>2</sup>	Char yield, %	Layer char thickness, mm	$\rho_c$ , kg/m <sup>3</sup>
Starch, $\alpha = 0.5$	20	70.4	26.0	231
	30	63.2	28.0	229
	40	59.7	30.0	227
	50	–	31.0	226
Starch, $\alpha = 0.3$	20	50.4	7.0	260
	30	43.9	9.0	255
	40	39.6	11.0	248
Rice, $\alpha = 0.5$	20	68.3	17.0	239
	30	61.3	21.0	236
	40	57.4	24.0	233

All compositions confer Group II of fire protection efficiency to pine timber and the rank of hard flammable material even at consumption of 100 g/m<sup>2</sup>. As MP composition consumption increases to 300–400 g/m<sup>2</sup>, the mass losses during firing tests decrease considerably. Intumescent MP coatings confer Group I fire protection efficiency. In this respect, MP with  $\alpha = 0.5$  is more effective.

The degree of catalytic oxidation of polysaccharides affects the fire protection efficiency of coatings because of its impact on the progress of polymer decomposition and expansion, thickness of the expanded layer, and char yield and properties. For equal MP consumption of 300 g/m<sup>2</sup>, the thickness of charring foam increases as the intensity of radiative heat flow increases, whereas char mass yield decreases. At the same time, the density of the intumescent charred layer decreases slightly (Table 9.6).

An MP starch-based intumescent coating with oxidation degree  $\alpha = 0.5$  applied on pine timber increased the specimen's ignition time at radiative heat flow exposure  $q''_c = 30$  kW/m<sup>2</sup> to 670 s. Under these conditions, the ignition delay time of the untreated specimen was  $\tau_i = 21$  s. The MP coating based on rice grits with the same oxidation degree  $\alpha = 0.5$  increased ignition time only to 535 s. Ignition time decreases almost 2.5 times when the oxidation degree decreased to 0.3.

A similar effect of MP oxidation degree and type of initial raw material was seen when the critical density of ignition heat flow,  $q''_{cr}$ , maximum mass loss rate of fire protected timber specimens,  $MLR_{max}$ , and other parameters of timber fire safety were being determined (Sivenkov et al. 2002a, b, c).

An intumescent coating based on potato starch with oxidation degree  $\alpha = 0.5$  is the most effective. It raises the  $q''_{cr}$  value from 12.5 kW/m<sup>2</sup> for the initial pine specimen to 29.7 kW/m<sup>2</sup>. Maximum mass loss rate of timber at constant heat flow of 50 kW/m<sup>2</sup> decreases almost twofold (from 35.7 to 16.1 g/m<sup>2</sup>) (Sivenkov et al. 2002a).

In spite of the absence of any additional fire retardants, the organic intumescent MP-based coating efficiently protects timber from the exposure of fire. It lowers the flame spread index for the timber surface from 55 to 0.8.

The critical heat flow value, below which the flame stops spreading over the material surface and extinguishes, increases from 5 kW/m<sup>2</sup> for unprotected timber to 27.8 kW/m<sup>2</sup> for timber with a fire-retardant MP coating. Timber with this fire protection transfers to the category of slow flame spreading materials (FS 1).

As can be seen from Fig. 9.1, the intumescent starch MP-based coating has a significant effect on smoke generation during timber combustion. With equal consumption of KSD-A (g.1) impregnation composition, it further reduces the smoke generation coefficient during pine timber combustion with external heat flows of 18–35 kW/m<sup>2</sup> (Sivenkov et al. 2002b; Aseeva et al. 2007).

The same situation may be seen in examining the effect of a starch MP coating on timber combustion product toxicity (Fig. 9.2).

According to the recognized classification, an intumescent starch MP-based coating moves timber to the group of materials with moderate smoke generation capacity (D2) and in terms of combustion product toxicity, from the rank of highly hazardous materials (T3) to the group of moderately hazardous (T2) at heat flows up to 32 kW/m<sup>2</sup>.

When a starch MP-based composition with  $\alpha = 0.5$  and consumption of 300 g/m<sup>2</sup> is applied to a timber surface, the resulting coating lowers the maximum and average heat release rate during timber combustion at external heat flow of 50 kW/m<sup>2</sup> almost 3.5-fold compared to an untreated specimen (Sivenkov et al. 2002c).

The mechanism of timber fire protection by MP intumescent coatings consists in the formation on the timber surface of char foam with low-density and low-thermal inertia ( $k\rho c = 0.0626 \text{ kJ}^2/\text{m}^4\text{K}^2\text{s}$ ).

A layer of this char foam with high thermal insulating properties is a barrier to heat transfer to the timber surface and lowers the probability of its pyrolysis and charring. The charring rate of timber with an MP coating at an external heat flow of 50 kW/m<sup>2</sup> was only 0.18 mm/min (Sivenkov 2002).

How does fire protection efficiency of the two applied systems depend on the variety of timber being protected? To answer this question, the heat release characteristics during combustion of pine, spruce, birch, and oak specimens were analyzed. An OSU HRR-3 calorimeter was used with external radiative heat flow of 35 kW/m<sup>2</sup> for this purpose. Fire-retardant compositions with total consumption of 400 g/m<sup>2</sup> were applied on the surface of timber specimens with dimensions of 150 × 150 × 10 mm (Aseeva et al. 2009b).

It was found that fire-retardant composition KSD-A (grade 1) and an intumescent coating based on starch MP with  $\alpha = 0.5$  increase the time of heat release onset from the moment of external heat exposure, as well as the time to reach the maximum heat release rate. Both fire-protective systems significantly lower the maximum heat release rate and total heat release during the first 2 min of timber combustion.

It was confirmed that in comparison with impregnation composition KSD-A, the composition based on modified polysaccharides demonstrates higher fire protection efficiency due to the formation of a thick expanded coke layer with high thermal insulating properties. In this case, the effect of timber variety is more obvious, especially in terms of total heat release. Thus, an intumescent coating on the surface of pine and fir timber specimens based on modified polysaccharides resulted in a

1.8-fold and 3.2-fold decrease in total heat release  $THR_{2min}$ , respectively. When the intumescent coating was applied on the surface of oak and birch specimens, total heat release in this period decreased 3.8 and 9.3 times, respectively, compared to the specimens of untreated timber. This parameter was least affected by timber variety, when KSD-A impregnation composition was used:  $THR_{2min}$  value decreased 1.5–2-fold for all timber varieties.

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